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PATENT SPECIFICATION



Application Date: June 30, 1933. No. 18606/33.

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PROVISIONAL SPECIFICATION

Manufacture of new Rhodamine Dyes and their application

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W. 1, a Company incorporated under the laws of Great Britain and MAX WYLER, a Swiss Citizen, of Hexagon House, Blackley, Manchester, do hereby declare the nature of this invention to be as follows:—

Neither naphthalene-2:3-dicarboxylic acid nor its anhydride has hitherto been used for the manufacture of rhodamine dyes. We have now found that they may replace phthalic acid or anhydride in the manufacture of rhodamines by known methods from derivatives of *m*-aminophenol having one or both hydrogen atoms of the amine group substituted by alkyl or aryl groups. The resulting new rhodamine colours are similar in shade to the corresponding known rhodamines from phthalic acid, but are insufficiently soluble in water to be valuable in textile dyeing, although they can be used as lakes. We have found however that they can be sulphonated with ease and that the sulphonated products are acid dyes which for instance dye wool in brilliant shades of good to very good general fastness.

The following Examples in which parts are by weight illustrate but do not limit the invention.

EXAMPLE 1.

21.6 Parts of naphthalene-2:3-dicarboxylic acid, 16.5 parts of diethyl-*m*-aminophenol, and 10.0 parts of fused zinc chloride are mixed and heated gradually to 200° C. and kept at this till the melt becomes nearly solid. The melt is allowed to cool, ground and extracted with warm water to remove zinc salts. The resulting insoluble matter is then stirred at 50° C. with 100 parts of 10% aqueous caustic soda, filtered, washed and recrystallised from toluene. The resulting base is in beautiful orange-coloured needles. It can be converted to sulphate by dissolving in boiling dilute sulphuric acid and then adding a little sodium chloride to convert the resulting gelatinous product into crystals. It dyes tannin mordanted cotton in the same shade as Rhodamine B but it is not suffi-

ciently soluble to find practical application in this way.

Sulphonation is effected by dissolving the melt after water washing and drying, in 150 parts of 100% sulphuric acid below 20° C., adding 40 parts of 60% oleum below 60° C. and keeping at 60° C. until a sample is completely soluble in soda ash solution. The sulphonation mixture is poured into 1000 parts ice water, filtered, wash-free from acid, dried and mixed with 20% of its weight of soda ash.

It dyes wool brilliant bluish-red with outstanding levelling and fastness properties.

EXAMPLE 2.

By replacing in Example 1 16.5 parts diethyl-*m*-aminophenol by 13.7 parts of monoethyl-*m*-aminophenol, but otherwise proceeding in the same manner a more insoluble product is obtained, the sulphate of the base being very insoluble even after esterification. The base is sulphonated as in the previous example and the resulting product dyes wool a bright red-orange shade of very good fastness.

EXAMPLE 3.

Instead of 16.4 parts of diethyl-*m*-aminophenol in Example 1, 15.1 parts of ethylamino-*p*-cresol are taken. After the melt has been washed free from zinc chloride and the product decomposed with dilute caustic soda solution and dried, the base is esterified in the following way: 10 parts of base are dissolved in 40 parts of 100% sulphuric acid, 300 parts of ethanol are added and heated under reflux at 100° C. for 12 hours. The reaction product is poured into 500 parts of water, filtered and dissolved in 750 parts of boiling water, and the solution left to crystallise. The new rhodamine separates in lustrous green crystals. It dyes and prints tannin-mordanted cotton in shades very similar to but slightly brighter than Rhodamine 6GBS. It is insufficiently soluble to find practical application.

By sulphonating the zinc free melt in exactly the same manner as described in Example 1 a colour is obtained which dyes wool fast red.

[Price 1/-]

Price 4s 6d

Dated the 30th day of June, 1933.

E. C. G. OLARKE,
Imperial Chemical House,
Millbank, London, S.W. 1,
Solicitor for the Applicants.

COMPLETE SPECIFICATION

Manufacture of new Rhodamine Dyes and their application

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W. 1, a Company incorporated under the laws of Great Britain and MAX WYLER, a Swiss Citizen, of Hexagon House, Blackley, Manchester, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

Neither naphthalene-2:3-dicarboxylic acid nor its anhydride have been used for the manufacture of rhodamine dyestuffs. We have now found that they may replace phthalic acid or anhydride in the manufacture of rhodamines, by methods known per se, from N-alkyl- or NN-dialkyl-aminophenols. The resulting new unsulphonated rhodamine dyestuffs are similar in shade to the corresponding known rhodamines from phthalic acid, but are insufficiently soluble in water to be valuable in textile dyeing, although they can be used as lake-colouring matters. We have found, however, that they can be sulphonated with ease by known methods and that the sulphonated products are acid dyes which for instance dye wool in brilliant shades of good to very good fastness.

The following Examples in which parts are by weight illustrate but do not limit the invention.

EXAMPLE 1.

21.6 parts of naphthalene-2:3-dicarboxylic acid, 16.5 parts of diethyl-*m*-aminophenol, and 10.0 parts of fused zinc chloride are mixed and heated gradually to 200° C. and kept at this till the melt becomes nearly solid. The melt is allowed to cool, ground and extracted with warm water to remove zinc salts. The resulting insoluble matter is then stirred at 50° C. with 100 parts of 10% aqueous caustic soda, filtered, washed and recrystallised from toluene. The resulting base is in beautiful orange-coloured needles. It can be converted to sulphate by dissolving in boiling dilute sulphuric acid and then adding a little sodium chloride to convert the resulting gelatinous product into crystals. It dyes shad as Rhodamine B but it is not sufficiently soluble to find practical application in this way.

Sulphonation is effected by dissolving the melt after washing with water and drying, in 150 parts of 100% sulphuric acid below 20° C., adding 40 parts of 60% oleum below 60° C. and keeping at 60° C. until a sample is completely soluble in soda ash solution. The sulphonation mixture is poured into 1000 parts ice water, filtered, and the orange-coloured product is washed free from acid, dried and mixed with 20% of its weight of soda ash.

It dyes wool brilliant bluish-red shades having outstanding levelling and fastness properties.

EXAMPLE 2.

By replacing in Example 1, 16.5 parts of diethyl-*m*-aminophenyl by 13.7 parts of monoethyl-*m*-aminophenol, but otherwise proceeding in the same manner a more insoluble product is obtained, the sulphate of the base being very insoluble even after esterification. The base is sulphonated as in the previous example and the resulting product dyes wool a bright red-orange shade of very good fastness.

EXAMPLE 3.

Instead of 16.5 parts of diethyl-*m*-aminophenol in Example 1, 15.1 parts of 2-ethylamino-*p*-cresol (OH, = 1) are taken. After the melt has been washed free from zinc chloride and the product decomposed with dilute caustic soda solution and dried, the base is esterified in the following way: 10 parts of base are dissolved in 40 parts of 100% sulphuric acid, 300 parts of ethanol are added and heated under reflux at 100° C. for 12 hours. The reaction product is poured into 500 parts of water, filtered and dissolved in 750 parts of boiling water, and the solution left to crystallise. The new rhodamine separates in lustrous green crystals. It dyes and prints tannin-mordanted cotton in shades very similar to but slightly brighter than Rhodamine 6GBS. It is insufficiently soluble to find practical application.

By sulphonating the zinc free melt in exactly the same manner as described in Example 1 a colour is obtained which dyes wool fast red.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of new colouring matters of the rhodamine series which comprises condensing naphthalene-2:3-dicarboxylic acid or its anhydride with an *m*-aminophenol in which the nitrogen atom carries one or two alkyl groups.
2. Process for the manufacture of new colouring matters of the rhodamine series which comprises a process as claimed in Claim 1 followed by sulphonation of the product, e.g. with oleum.
3. Process for the manufacture of new colouring matters of the rhodamine series substantially as described with reference to each of the foregoing Examples.
4. New colouring matters of the rhodamine series whenever produced by the process of any of the preceding claims, or by the obvious chemical equivalent of such process.

Dated the 19th day of June, 1934.

E. C. G. CLARKE,
Imperial Chemical House,
Millbank, London, S.W. 1,
Solicitor for the Applicants.

